Alan's Tips

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Be patient

The single most important thing about making Chlorates or Perchlorates is patience. Run-times tend to be 1-2 weeks, as cells with passive cooling can't take much more than 1-2 Amp per 100 ml. Purification of Potassium Perchlorate will take *at least* three crystallisation cycles to achive a purity sufficient for good pyrotechnic blues. This takes several days of part-time work as you can only do 1-2 cycles a day because of the cooling time. This also involves a large volume of water and evaporating the supernatant liquid to recycle what is dissolved in it will take an hour or two per cycle.

pH control isn't a big deal

You will get more efficiency benefit for less engineering hassles by keeping the Chloride concentration up than maintaining the pH precisely. To do pH control properly you will need a closed-loop system, you can't just add some HCl each day or rely on a syringe pump or similar metered dosage system. The pH will stabilize fairly alkaline and the efficiency remain better than 50% as long as the Chloride concentration is kept above 300 g/l.

Keep Chloride/Chlorate concentration high

Not only will doing so keep your cell's electrochemical efficiency and electrical conductivity high, it will minimise wear on your anodes. The simplistic method is to run your cell only to 100g/l of Sodium Chloride or Sodium Chlorate rather than to complete consumption of the Chloride or Chlorate. Those last 100g/l will be at terrible efficiency and at the cost of much wear on the anode.

A better but more complex method is to re-saturate the liquor continuously as the cell runs. This may be achieved simply by extra solid input material left undissolved on the bottom of the cell. It will be slowly consumed as the cell runs, and will "salt-out" the product and exchange places with it. This complicates taking out the product if you don't run the cell long enough to consume most of the input chemical. However you can simply decant the warm liquor and allow it to cool, taking whatever product crystallises out then re-saturate by pouring it back into the cell. The stuff on the bottom of the cell is replenished when it starts getting thin.

The yields will seem small at first, especially for Sodium Chlorate cells because of high solubility of Sodium Chlorate, however over time this is one of the easiest processing methods. It can be arranged into a continuous process, by pumping a quantity of warm liquor into a crystallising chamber where it cools and then decanting off the liquor where it is fed back into the cell to re-saturate from material on the cell floor (or through a re-saturator before injecting back into the cell).

Don't waste your Platinum

If you have Platinum anodes available don't waste them in Chlorate cells unless you are keeping them continuously re-saturated to avoid wear on the anode. It is best to keep Platinum for Perchlorate production, strong low-Chloride solutions of Sodium Perchlorate are the best feedstock for a Perchlorate cell with a Platinum anode. Similar to the case with Chlorate cells continuous re-saturation will help prevent anode ware and keep the electrochemical efficiency back up.

Use KCl if you only need KClO3

Despite its somewhat lower electrochemical efficiency a Potasium Chlorate cell is much more straight forward and skips the frustrating process of removing the Sodium from the product. Like a Sodium Chlorate cell it can be continuously re-saturated with Potassium Chloride which will keep the efficiency up, and Potassium Chlorate will precipitate out as the reaction proceeds. If you are using MMO anodes in most cases a simple re-crystallisation to remove any stray Chloride is all that will be needed.

You may leave an inch or two of KCl crystals on the bottom of the cell, they will be slowly replaced by KClO3 over time while keeping the Cl- concentration and electrochemical efficiency high and anode wear low. Knowing when to stop and process the crystals and replenish the KCl can be a matter of guess work unless you have a good idea of the efficiency of your cell. After a few cycles you will know when there is little Chloride left and its time to process the crop. You can use Silver Nitrate to estimate the Chloride concentration, if it is below 100 g/l it is time to do a cycle before the anode starts to wear.

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Graphite is a b*tch

Ohmic losses in the graphite and at its connection point with the wiring will give you lots of grief. Even with Silver epoxy or plating the heating at the graphite/Cu interface will often destroy the electrode mounting assembly. The heating inside graphite anodes above the solution tends to dry the fine spray of electrolyte, causing crusting and creeping of electrolyte up to the electrical connections and speeding their destruction. The crust of chlorate-heavy salts will rapidly react with the binders in some graphite rods, causing them to break off and fall into the solution ruining the cell.

Combined with the slow erosion of graphite into the liquor and the huge pain it is to filter it out you will probably rapidly loose your patience with graphite and start looking for alternatives in your Chlorate cells. That said, graphite is cheap and easily obtained and is all you need for making Chlorate.

Use good quality labware

Destruction of residual Chlorate requires lowering the pH significantly. In poor-quality stainless pots this will contaminate the liquor with Iron Chloride, in fact even the best quality pots don't like the nasty liquor much and it is best to use borosilicate glassware for handling liquor that hasn't been processed and neutralised. The Iron Chloride itself isn't a big deal, you can selectively remove it during crystallisation, but once you add Sodium or Potassium Hydroxide to raise the pH back towards neutral Hydrated Iron Oxide/Hydroxide will be precipitated in an extremely fine form that is near impossible to filter out. The Iron Hydrates will stain your product and be quite difficult to remove.

Iron Hydrates can be removed from Potassium Perchlorate by dissolving it with Hydrochloric Acid. Do this either by washing in a filter with HCl or by adding HCl to a re-crystallisation cycle until the Iron Hydrate flocculate dissolves completely leaving a clear greenish yellow solution. This will not decompose Potassium Perchlorate which can be re-crystallised leaving the Iron Chloride in the acidic solution. The solid Perchlorate can then be washed clean of Iron then further purified by more cycles of re-crystallisation during which any residual acidity is neutralised with a Hydroxide.

Obviously this can't be attempted with Chlorates as the low pH will cause decomposition of the Chlorate. Coagulation of the Iron into its Hydroxide/Hydrate by taking the pH very alkaline and boiling may allow filtering out of a large part of the Iron contamination from Chlorate liquors before crystallisation.

Precipitation of Potassium Perchlorate is exothermic

When you add Potassium Chloride solution to the Sodium Perchlorate liquor to precipitate Potassium Perchlorate ensure at least one of the solutions is cold. The reaction is exothermic, and if both solutions are near boiling the energy release may very well cause a local boiling event and spray you with extremely hot crystal slurry. You get a better yield if the solution is cold anyway, so I recommend cooling both solutions first. stirring briskly is a good idea, it dissipates the heat and ensures a complete reaction. Thermal and density effects can cause seperation of the reactants into layers that will react only very slowly at the interface if you just tip the Chloride solution into the Perchlorate one and leave it, especially if the Chloride one is warm - you will get a creamy precipitation instantly that will float because of the heat generated, then slowly sink, separating from the Perchlorate depleted liquor and leaving Chloride rich liquor on top.

Some plastics are soluble in the liquor

Polyethene in particular will partially dissolve into the hot caustic solution rich in Chlorine/Oxygen radicals. You may find if you use PE that a slimy deposit of it will form on the cathode reducing the conductivity of the cell somewhat. Dissolved material will also come out as a floc when the pH is lowered during liquor processing. This can be especially difficult to filter out as it blocks filters very easily.

Some filter materials (Cellulose) also partially dissolve into the raw cell liquor, only to precipitate Viscose when the pH is lowered. Viscose flocculate also easily blocks filter membranes, frustrating attempts to filter it out.

PE /is/ a usable material for a cell, it won't fail completely, but its side effects are annoying. Chlorinated polymers are much more stable, common PVC is an excellent choice, as is Polypropylene. Stainless steel is usable, but must be bonded to the Cathode to protect it.

3 comments.

Parent article: Making Chlorates and Perchlorates.

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